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DIFFUSION OF SULFUR IN IRON

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DIFFUSION OF SULFUR IN IRON

ABSTRACT

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In order to resolve the conflict in values given in the literature for the diffusion coefficient of sulfur in α - and γ -iron, experiments have been conducted with a heavy sulfide layer (constant diffusion source) and high-grade iron. The diffusion coefficients are calculated by the standard plot method. The results indicate distribution of the sulfur along the grain boundaries as point inclusions, with boundary diffusion proceeding via intergranular strata of the iron. Practically the same diffusion coefficient (1.6 and $1.3 \cdot 10^{-9} \text{ cm}^2/\text{sec}$, respectively) is obtained in γ -iron and α -iron single crystals, the latter having a lesser imperfection of the crystal structure and fewer dislocations in the less disordered intergranular strata.

Author

Qualitative data on the diffusion rate of sulfur in iron were obtained [311*] some time ago by Ziegler (ref. 1) and Fry (ref. 2). Numerical values were found some time later for the diffusion coefficients of sulfur in commercial iron in the temperature interval from 950 to 1150°C (ref. 3). For the diffusion parameters of sulfur in γ -iron, however, disparate values are given: according to Barrer (ref. 4), $D_0 = 4.8 \cdot 10^{-6} \text{ cm}^2/\text{sec}$, $Q = 23,400 \text{ cal/mole}$; according to Seith (ref. 5), $D_0 = 1.6 \cdot 10^{-5} \text{ cm}^2/\text{sec}$, $Q = 26,700 \text{ cal/mole}$.

*Numbers in the margin indicate pagination in the original foreign text.

The values obtained in reference 3 for the diffusion coefficients of sulfur in iron are normally given in the literature as the volume coefficients of sulfur in γ -iron. The latter are clearly not quite consistent with reality. /312

The concentration of sulfur in these experiments was 0.5-0.7% at the surface of the samples and about 0.02% in the depth of the diffusion layer, which is an order of magnitude higher than the saturation solubility of sulfur in iron in the given temperature interval (ref. 6). Data presented in reference 3 from a laminar analysis of one of the iron samples fit fairly well on a straight line $\ln c = i(x)$, which evinces predominantly boundary diffusion. Consequently, the data presented in reference 3 comprise certain effective values of the diffusion coefficients for sulfur primarily via the intergranular strata of iron.

In view of the low purity of the initial iron samples (sulfur content 0.04%) and the relatively low temperatures, our earlier experimental data on the diffusion of sulfur in iron (ref. 7) also represent more or less effective values of the diffusion coefficients for sulfur predominantly via the intergranular strata of iron.

We subsequently investigated the diffusion of sulfur in high-purity iron. In the initial samples, spectral analysis disclosed only traces of foreign metals, and the content of carbon, phosphorous, sulfur, and nitrogen amounted to 0.003-0.004% as indicated by chemical analysis. The investigations were conducted at high temperatures (1150 to 1250°C) so as to preclude more rapid boundary diffusion. The source of diffusing sulfur atoms was a relatively thick layer ($\sim 5\mu$) of iron sulfide on the surface of the samples, so that the diffusion would originate from a constant source. Diffusion annealing was conducted in sealed quartz ampules in vacuum (10^{-3} mm Hg). The values of the diffusion coefficients, calculated by the standard plot method (ref. 8), are shown in

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Figure 1. Their temperature dependence is described by the following equation:

$$D = 1.8 \cdot 10^{-2} \exp (-38,600/RT) \text{ cm}^2/\text{sec.}$$

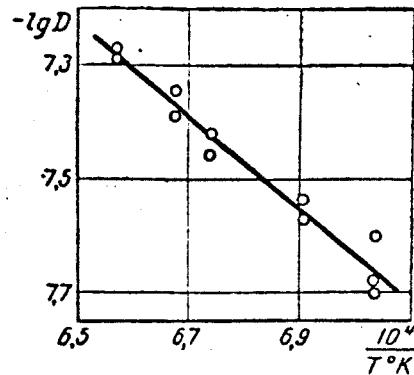


Figure 1. Temperature Dependence of the Diffusion Coefficients of Sulfur in γ -Iron.

The activation entropy, determined by the method of Wert and Zener (ref. 9),

turned out to be positive and practically equal to unity.

The sulfur distribution during its diffusion in the γ -iron is shown in

figure 2a. Against the background of the uniform distribution are singular point inclusions of sulfur. They appear to be spaced along the grain boundaries of the metal. This is borne out by figure 2b. In this case, at certain sites of the solid network of predominantly boundary distribution, with a concentration somewhat higher than in the grains, regions are encountered where the boundary segregation of sulfur is sharply delineated. In diffusion from a very thin sulfide layer, i.e., from a variable source, in iron as well as other metals (refs. 10 and 11), at high temperatures the sulfur was distributed uniformly throughout the entire volume. Despite the presence of point inclusions, the experimental curves for the distribution of sulfur in γ -iron samples correspond to the theoretical. The same effect is also observed in the diffusion of sulfur in ferrosilicon alloy (ref. 12).

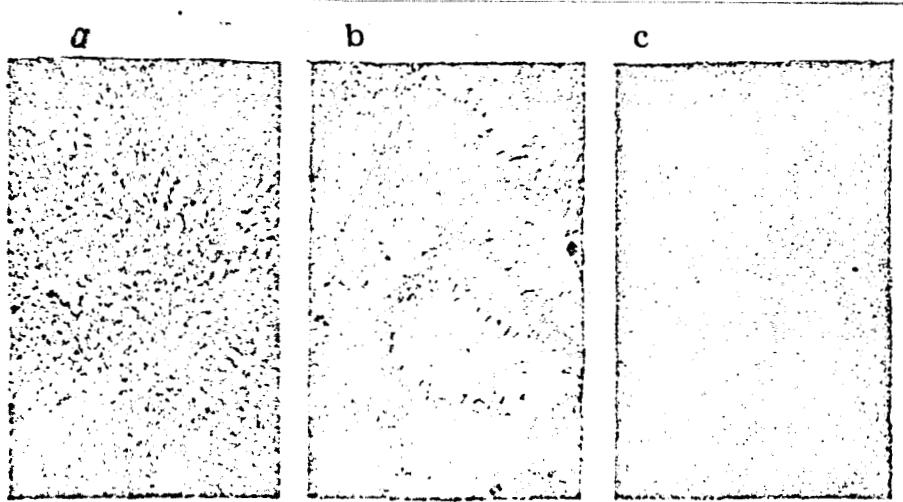


Figure 2. Distribution of Sulfur in Iron. X 90.

- a) γ -Iron, 1175° , depth $\sim 20 \mu$; b) γ -Iron, 950° , depth $\sim 20 \mu$;
 c) γ -Iron, 850° , depth $\sim 100 \mu$.

We were unable to investigate the volume diffusion of sulfur in α -iron, because even at 850-900°C boundary diffusion prevailed in depth of the diffusion layer, as evinced by figure 2c. At the surface of the α -iron samples there existed a uniform sulfur distribution. Owing to the influence of boundary diffusion at 900°, the last two or three points in the depth of the diffusion layer depart from the theoretical standard curve. The sulfur diffusion coefficient at this temperature turned out to be equal to $(1.6 \pm 0.1) \cdot 10^{-9} \text{ cm}^2/\text{sec}$. If we take into account the accelerating influence of the boundary diffusion, the latter agrees almost completely with the diffusion coefficient of sulfur in α -iron single crystals for the given temperature ($1.3 \cdot 10^{-9} \text{ cm}^2/\text{sec}$, ref. 12). Furthermore, the values of the diffusion coefficients for sulfur in both modifications at the phase transition point turn out to be approximately identical in commercial iron (ref. 7) as well as in high-purity iron.

The same situation is noted in the diffusion of boron in iron (ref. 13),
which is clearly attributable to the characteristics of the diffusion of sulfur
and boron atoms via the interstices of the cubic lattices of α - and γ -iron.

[313]

The self-diffusion and diffusion coefficients of the majority of other elements
in γ -iron is three or four orders of magnitude less than in α -iron.

The grain boundaries of α -iron were only slightly more enriched with sulfur
than the grains, and point inclusions, as in γ -iron (fig. 2a, 2b) were not
observed at all. The experimental procedure in both cases was the same, except
that before investigating the diffusion of sulfur in the α -phase the initial
iron samples were given a second anneal in vacuum for nine hours at 890°C.

The differences in the distribution of sulfur in α - and γ -iron are clearly
related to a certain difference in the structure of the grain boundaries of
these modifications. As a result of phase transition ($\alpha \rightarrow \gamma$), the region of
intergranular stratification in γ -iron proves to be more disordered and, there-
fore, has greater imperfections of the crystal structure and a higher concentra-
tion of dislocations than the intergranular stratification region of α -iron.

I express my gratitude to Prof. M. M. Pavlyuchenko and Prof. P. L. Gruzin
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Belorussian State University (V. I. Lenin)

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